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Assessment of Trace Estrogenic Contaminants Removal by Coagulant Addition, Powdered Activated Carbon Adsorption and Powdered Activated Carbon/Microfiltration Processes

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Abstract: Increasing attention is being paid to health and environmental risk as a result of the presence of trace steroid estrogens in the effluent discharged from municipal sewage treatment plants. This paper focuses on assessment of removal of these trace compounds using ³H-labelled estrone as the model compound. Jar tests over a range of ferric chloride dosage and pH conditions showed that coagulation was ineffective in removal of estrone from secondary effluent. The experiments showed that the combination of PAC and microfiltration could be effective for removal of trace estrone from water. The rate and extent of estrone removal by PAC are functions of PAC dosage and retention time of PAC in the system. Mathematical analysis of the results using a homogeneous surface diffusion model (HSDM) indicates that the adsorption of estrone on PAC can be limited by film diffusion and internal surface diffusion. The surface and film mass transfer coefficients were determined to be $9.72 \times 10^{-10} \text{ cm}^2/\text{min}$ and $1.963 \text{ cm}/\text{min}$, respectively, under the conditions used.

Keywords: Estrogenic compound; Adsorption; Coagulation; Hybrid membrane process.

Introduction

Endocrine disrupting and pharmaceutically active compounds which are excreted by humans and enter the environment via effluent discharge from municipal sewage treatment plants (STPs) may have significant impacts on both biota exposed in the receiving environment and human health (Ternes 1999; Hirsch 1999; Körner 2000). Although field data suggests that modern activated sludge treatment processes could consistently remove most of the synthetic and natural hormones that enter the works (Johnson and Sumpter 2001), steroid estrogens such as estrone and estradiol still occur at significant concentrations in sewage effluent (Johnson and Sumpter 2001). These trace compounds, usually present in the range of 1 to 30 ng/L, could exert significant effects on biota exposed in the receiving environment (Sumpter and Jobling 1995).

One of the possible solutions to enhancing removal of endocrine compounds from secondary effluent is to combine low-pressure membrane processes such as UF or MF with other physicochemical processes in so-called hybrid membrane processes. In such systems, MF or UF membranes can be a positive barrier for various particulates including clays, metal oxides, algae, bacteria, and parasites such as *Cryptosporidium* and *Giardia*, while adsorption to added particulates or hydrolyzable coagulants could be effective for removal of dissolved organics. The widely used physicochemical processes in water treatment include activated carbon adsorption and coagulation. Adsorption to hydrolyzable coagulants is often very effective in removing acidic and basic components of the dissolved organic matter in natural waters provided pH conditions and dosage are properly controlled (Dennett et al. 1996). Randtke and McCarty (1979) assessed the potential of various physicochemical processes for the removal of soluble secondary-effluent organics and demonstrated that activated carbon adsorption is generally the most proficient in removal of soluble organic matter. Morris and Weber (1964; 1969) presented a considerable amount of data on the adsorption of phenol, sodium salts of sulfonated organics, and pesticides. The kinetics of adsorption of organics on activated carbon have also been extensively studied by a number of investigators (Weber and Chakravorty 1974; Traegner and Suidan 1989; Roy et al. 1993; Najm 1996; Knappe et al. 1998). Research has also been undertaken showing that the combination of MF/UF with coagulation or carbon adsorption could be very effective for organic removal in tertiary wastewater or drinking water treatment. Lee et al. studied removal of phenol by adsorption on powdered activated carbon in a continuous flow stirred cell membrane system and reported that the kinetic behavior of the system can be well described by a surface diffusion model (Lee et al. 1997). Campos et al. developed mathematic models based on HSDM for PAC-membrane filtration processes with different process arrangements and verified that these models can be used to predict trace organic removal by the combined membrane PAC systems (Campos et al. 1997; 2000a,b). Best et al. reported that a single tank coagulation-submerged ultrafiltration processes was effective for colour and TOC removal from natural water (Best et al. 1999). Pirbazari et al. (1992) reported that high organic removal from water contaminated with natural and synthetic organics can be achieved by combined MF-PAC processes. Similar results with submerged PAC-MF system have also been reported by other researchers (Lebeau et al. 1998; Suzuki et al. 1998).

In this paper, the further removal of trace steroid estrogens by coagulation, PAC adsorption, and PAC-microfiltration processes has been investigated with different background solutions spiked by ³H-labelled estrone through jar test, flask adsorption, and stirred cell filtration studies, respectively. The effects of dosage of ferric chloride and pH on estrone removal, the PAC adsorption isotherm relationship and effect of competitive adsorption, as well as removal rate of estrone by the combined PAC-membrane system have been investigated. In addition, the homogeneous surface diffusion model (HSDM) has been used to assess the mechanisms of mass transfer of estrone adsorption to PAC.

Experimental materials and methods

Adsorption of estrone to hydrolyzable coagulants was investigated through use of a conventional jar-test apparatus. Regular grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was applied at various dosages (5 - 50 mg/L) and pH conditions (5-11.4) into four beakers containing 100mL secondary effluent spiked with estrone (at about 15ng/L). The coagulation protocol involved rapid mixing at 100 rpm for 3 minutes, followed by slow mixing at 30 rpm for 30 minutes. Then, after settling for 60 minutes, the samples were taken from the supernatant. Some of the samples were further treated by filtration using a PLHK membrane (MWCO, 100 kDa, Millipore) to assess the removal of estrone with different methods of sample treatment.

Flask adsorption experiments were performed to assess the removal capacity of powdered activated carbon for estrone. In these experiments, 50 mL background solution in the flasks was spiked to an

estrone concentration of 100 ng/L and different amounts of PAC (0.5 – 50 mg/L) were added to the flasks. The adsorption experiments were conducted in an incubator (Bioline, Edwards Instrument Company Australia) under conditions of 250 rpm mixing speed and 25 °C for 48 hours enabling equilibrium to be reached. The powdered activated carbon (Norit SAM 52) was provided by Swift, Melbourne. The median particle size (D_{50}) of the PAC is 20 µm and has a total surface area (BET) of 72.5 m²/g and density 450 kg/m³.

The PAC-MF filtration system used in this study is shown in Figure 1. The system consists of a stirred cell, a magnetic stirrer (Amicon), suction pump, pressure transducer, and computer data collection system. The filtration has been carried out in constant flux mode with the permeate drawn through the membrane by the peristaltic pump and recirculated to the open stirred cell. The cell has an effective volume of 200mL and a certain amount of PAC was directly added into the cell during the experiments. The suction pressure was measured by a pressure transducer. The samples were taken either from the permeate side or both the permeate and feed sides at a certain time intervals as required. The membrane used in the filtration experiments was a hydrophilic GVWP membrane (Millipore) which has a nominal pore size of 0.22 µm. A new membrane was used for each experiment.

Background solutions of either 1mM NaHCO₃ and 20 mM NaCl buffer (which provided buffering to about pH 8) or secondary effluent were used. The effluent (TOC 13.2 mg/L, pH 7.2 to 7.5) was taken from St Marys Sewage Treatment Plant, NSW, Australia. Test solutions were prepared by dissolving a certain amount of ³H-labelled estrone in the background solutions. The radiolabelled estrone was purchased from Sigma Aldrich (Saint Louis, Missouri, USA). A Packard Instruments scintillation counter which has a detection limit of approximately 0.1 ng/L was used for analysis of the radiolabelled compounds. A TOC-5000A (Shimadzu) total organic carbon analyser was used to analyse TOC in the solutions tested.

Results and discussion

Estrone removal by adsorption to hydrolysable coagulants

Adsorption to hydrolysable metal salts is effective for removal of dissolved organic matter (DOM) from water. The metal ions which exist in aqueous phase as aquometal complexes can be hydrolysed to positive or negative hydroxocomplexes depending on pH conditions. These hydrolysis products destabilize colloids in two ways: either by adsorption and charge neutralization, or by enmeshment in a sweep floc (Stumm and O'Melia 1968). In this study the effect of coagulation on estrone removal was assessed through jar test experiments using FeCl₃ as coagulant and secondary effluent as a background solution that was spiked with estrone to a concentration of 15 ng/L. Figure 2 a shows the estrone concentration before and after coagulation with non-adjusted initial pH (pH = 7.5) and different dosages of FeCl₃. The samples after coagulation were taken from the supernate after settling the solution for one hour. Although a significant amount of floc formed during all the experiments and about 28% and 50% TOC removal was achieved for ferric chloride doses of 20 and 50 mg/L, respectively, only about 2.3 to 5 % of the estrone was removed by adsorption to the precipitated coagulant. Figure 2 b shows that the estrone concentration before and after coagulation with different pH conditions and a dosage of 30 mg/L. Although the experiments showed that the removal of TOC could be significantly affected by pH, no obvious change in estrone removal was observed for coagulation under different pH conditions.

Figure 3 compares the results obtained with samples treated by coagulation + settling and coagulation + membrane filtration. The membrane used was a PLHK membrane (MWCO, 100 kDa, Millipore), which is assumed to only allow passage of dissolved organics. From this figure, it can be seen that the results for these different treatment methods are quite similar, suggesting that the estrone added remains in solution after the addition of hydrolysable metal salts.

The results of these studies show that there are negligible interactions between trace estrone, colloids, and coagulants. This scenario is quite different to those obtained with relatively high estrone concentration (0.1 µg/mL) where a significant interaction between estrone and clay particles was observed (Lai et al. 2000). This suggested that further delimitation of trace estrogenic contaminants could become more difficult due to the decrease potential of interactions with other molecules or colloids in water.

Estrone removal by powder activated carbon

The ability of activated carbon to remove trace estrone from water was assessed through flask adsorption experiments. Figure 4 shows the final equilibrium estrone concentration achieved during adsorption of estrone from buffer solutions initially spiked to 120, 70 and 15 ng/L estrone after 48 hour adsorption. The final equilibrium concentration decreased with increase in PAC dosage until a limiting final concentration was reached. For an initial estrone concentration of 120 ng/L, a final concentration of 3.8 ng/L was achieved. When such an equilibrium concentration was reached, increasing PAC dosage did not lead to any further decrease in the final equilibrium concentration. For initial concentrations of 70 and 17 ng/L, the final (equilibrium) concentrations achieved were about 2.5 and 0.57 ng/L, respectively. Comparison between the equilibrium concentrations achieved and the corresponding initial concentrations suggested that the maximum removal of estrone for initial concentrations of 120, 70 and 17 ng/L were consistently in the range of 96 to 97%. This suggests that about 3 to 4 % of estrone in the solutions was not removable by PAC. This conclusion was further confirmed by adding fresh PAC into the solutions after 48 hours of adsorption (by which time equilibrium adsorption had been achieved). Figure 5 shows the initial and final estrone concentrations for the second adsorption by different doses of PAC. No further removal of the residue of estrone was achieved by the second addition of fresh PAC.

The adsorption capacity of PAC can be characterized by the relationship between the concentration of estrone in the solution and that absorbed by PAC at the equilibrium state. Figure 6 shows the extent of adsorption of estrone to PAC over a range of estrone concentrations in both carbonate buffer solution and secondary effluent. The results obtained in carbonate buffer demonstrate show adsorption capacities ranging from about 1.0 to 17 ng/mg depending upon the concentration of estrone in solution with the results adequately described by a linear adsorption isotherm over the concentration range tested:

$$q_e = 1.093C_e \quad (1)$$

The results obtained using secondary effluent suggest that competitive adsorption may be reducing the adsorption capacity of PAC for estrone. For equilibrium dissolved estrone concentrations of 1.3 to 17.4 ng/L, the amount of estrone adsorbed from the effluent to the PAC at the equilibrium was about 0.3 to 5.7 ng/L; significantly lower than that achieved in carbonate buffer solution. Figure 7 shows that the extent of effect of the competitive adsorption on estrone adsorption was a function of PAC dosage. For adsorption at low PAC dosage, the final solution concentration of estrone is relatively high. A reasonable explanation of these results is that the equilibrium concentration of estrone is controlled by the adsorption site availability. For adsorption at relatively high PAC doses, the final equilibrium partitioning behavior is limited by exhaustion of removable estrone in the solution so that the effect of competitive adsorption decreases while at low PAC doses, the estrone must compete for a limited number of surface sites with other dissolved constituents.

Estrone removal by combined MF-PAC system.

The results presented in section 3.2 imply that the combination of membrane with PAC could be an effective process for trace estrone removal from water. In such a hybrid membrane process, PAC can be completely retained by the membranes and the retention time is independent of other process

parameters. The efficiency of removal of estrone by combined MF-PAC processes was tested by combining these two processes using a stirred cell system in a batch operation mode (Figure 1). In these experiments the permeate was drawn through the membrane at a flux of 78 L/m²hr and PAC was directly added into the stirred cell. Before adding PAC into the stirred cell the microfiltration membrane used exhibited about 10 % retention to estrone. Since the pore size of the membrane used here is much larger than that of the estrone molecules, the retention of this compound to the membrane could be attributed to adsorption. A detailed discussion on estrone adsorption to membrane surfaces is been presented in another paper [Chang et al., 2002].

Figure 8 shows the change in estrone concentration in the permeate after addition of different doses of PAC into the stirred cell containing estrone spiked solution. The results show that when the PAC dosage was lower than 20 mg/L the removal rate was a strong function of PAC dosage; in other words, a significantly higher removal of estrone at a certain time could be achieved with higher PAC dosage. Almost no difference in removal rate was observed for adsorption with PAC doses of 20 and 30 mg/L, indicating that the process was controlled by the concentration of estrone in solution rather than adsorption sites required. The results shown in Figure 8 also suggest that removal rate is a strong function of time. For PAC concentrations of 20 mg/L or higher, about 91 % removal was achieved in the first hour and maximum removal (96%) was reached in three hours. These results demonstrate that PAC dosage and its retention time are important factors in achieving the desired removal efficiency. Figure 9 compares estrone removal by PAC from secondary effluent and buffer solution at different PAC dosages. From the figure it can be seen that lower estrone removal was achieved with the effluent over the period of the tests, suggesting the presence of other organics not only impacted the removal degree but also removal rate.

Adsorption kinetics

As shown in Figure 10, removal of estrone by PAC adsorption comprises a number of transport steps, including bulk solution transport, external (film) transport, internal (pore) transport, and adsorption. Once the molecules reach the boundary layer around the activated carbon particles through bulk transport, they will diffuse through the stagnant film layer and are assumed to penetrate further into the particle by surface diffusion to the adsorption site. The adsorption rate can be limited by one or more than one transport steps involved. In a mixed system, the transport rate is usually limited by film diffusion and internal surface diffusion. For such systems, the homogeneous surface diffusion model (HSDM) can be used to describe the adsorption process (Weber and Chakravorty 1994; Roy et al. 1993; Traegner and Suidan 1989; Najm 1996). Table 1 shows basics equations and initial and boundary conditions involved in HSDM theory for closed batch adsorption.

Roy et al. (1993) developed a simplified solution for the HSDM using the orthogonal collocation techniques (using three orthogonal collocation points) and Laplace transformation, which can reduce the equations in Table 1 into five non-linear algebraic equations. For a linear isotherm relationship, the HSDM solution can be simplified to the following set of equation for cases with and without film diffusion:

For non-film diffusion limitation:

$$\frac{C_t}{C_0} = \frac{1}{1 + 3K \frac{M}{V} A} \quad (9)$$

where

$$A = 0.333 - 0.049 \exp[-143(\frac{4D_s}{d_p^2})] - 0.054 \exp[-40t(\frac{4D_s}{d_p^2})] \quad (10)$$

$$- 0.202 \exp[-9.87t(\frac{4D_s}{d_p^2})]$$

For surface and film diffusion limitation

$$\frac{C_t}{C_0} = \frac{1}{1 + 3K \frac{M}{V} \frac{Bi}{Bi + E} \frac{A}{Bi + E}} \quad (11)$$

where

$$E = 2.144 + 0.049 \exp[-12.9(\frac{4D_s}{d_p^2})] + 1.58 \exp[-40t(\frac{4D_s}{d_p^2})] \quad (12)$$

$$+ 2.01 \exp[-9.87t(\frac{4D_s}{d_p^2})]$$

$$Bi = \frac{K_f d_p C_0}{2D_s \rho_p q_0} \quad (13)$$

Bi is the non-dimensional Biot number and represents the ratio of the rate of transport across the liquid layer to the rate of diffusion within the particle. According to Roy et al (1993), for Bi << 1, film diffusion dominates the mass transfer, while for Bi >> 100, internal surface diffusion controls the mass transfer rate. A Biot number between 1 and 100 indicates that the process is limited by both mass transfer mechanisms.

The developed models can be used to determine the film diffusion coefficient (K_f) and surface diffusion coefficient (D_s) by minimizing the sum of the squares of the difference between the corresponding model solutions and experimental data collected from batch adsorption experiments; i.e.

$$\text{Minimize}[f(D_s, K_f)] = \sum_{i=1}^m [(\frac{C_t}{C_0})_{\text{measured}} - (\frac{C_t}{C_0})_{\text{HSDM}}]^2 \quad (14)$$

The hybrid PAC-membrane system tested here can be regarded as a closed PAC batch adsorption system if the effect of adsorption on the membranes is neglected. The diffusion coefficients for estrone adsorption on the PAC particles was assessed using the developed models and least square residues strategy based on the data obtained from five different initial concentrations and different times. The surface diffusion coefficient was determined to be 1.38 x 10⁻¹⁰ cm²/min for the case in which film diffusion limitation was neglected. When considering the uptake process to be limited by both the effect of film and surface diffusion, the surface diffusion coefficient and film mass transfer coefficient was determined to be 9.72 x 10⁻¹⁰ cm²/min, and K_f = 1.963 cm/min, respectively. The simulated and experimental C_t/C₀-t relationships are given in Figures 11 a, b show that both models can predict the total tendency of change in solution concentration to a reasonable accuracy, suggesting that internal surface diffusion is the major factor limiting the rate of adsorption of estrone to PAC. Comparing the C_t/C₀-t relationship simulated by the no-film diffusion limitation model (Figure 11 a) with that predicted by the model considering film diffusion (Figure 11 b), the former predicted a much sharper concentration decrease in the initial stages of uptake than that observed experimentally. Such a sharp initial decrease in concentration could be mitigated by film transport or even bulk transport. In fact, the calculation shows that the Biot number for estrone adsorption on PAC is about 4, suggesting that the process is limited by both film and surface

transport mechanisms. Note that since q_0 is proportional to C_0 , the Biot number and thus C_t/C_0 are expected to be independent of C_0 . That C_t/C_0 is independent of the initial estrone concentration used is confirmed in the experimental results shown in Figure 12.

Conclusions

In this paper, we have examined the removal of trace concentrations of the natural hormone estrone from water by coagulation, PAC adsorption and PAC-microfiltration membrane processes. The results of studies of estrone removal in the presence of hydrolyzing metal salts in secondary effluent show that there are negligible interactions between trace estrone and aquometal ions or their fine colloidal oxyhydroxide products. As a result, it appears that addition of hydrolysable metal salts is ineffective for trace estrone removal from secondary effluent. In comparison, the results of studies with powdered activated carbon demonstrated that trace estrone can be effectively removed from aqueous phase by PAC. The rate and extent of estrone removal by the PAC are a function of PAC dosage and retention time of PAC in the system. More detailed analysis of rate of adsorption of estrone by PAC using HSMD models suggests that the adsorption process is limited by both film diffusion and internal surface diffusion. The surface and film diffusion coefficients were determined to be $9.72 \times 10^{-10} \text{ cm}^2/\text{min}$ and $1.963 \text{ cm}/\text{min}$, respectively, for the system examined.

Symbols

B_i = Biot number

C_e = equilibrium liquid phase adsorbate concentration at solid-liquid interface (ML^{-3})

C_0 = initial liquid phase concentration (ML^{-3})

C_s = liquid phase adsorbate concentration at solid-liquid interface (ML^{-3})

C_t = bulk liquid phase adsorbate concentration (ML^{-3})

d_p = adsorbate particle diameter (L)

D_s = surface diffusion coefficient ($\text{L}^2 \text{ T}$)

K = Freundlich isotherm capacity constant, dimensions vary with n

K_f = liquid film mass transfer coefficient (LT^{-1})

M = total mass of carbon in closed batch test (M)

n = Freundlich isotherm intensity constant (dimensionless)

$q(r,t)$ = adsorbed phase adsorbate concentration (MM^{-1})

q_e = equilibrium average adsorbed phase adsorbate concentration (MM^{-1})

q_0 = reference adsorbed phase adsorbate concentration corresponding to the initial liquid phase concentration (MM^{-1})

q_{avg} = average adsorbed phase adsorbate concentration (MM^{-1})

$q_s(t)$ = adsorbed phase adsorbate concentration at solid-liquid interface (MM^{-1})

ρ_p = apparent particle density (ML^{-1})

r = radial coordinate radial coordinate

t = time (T)

V = liquid volume in close batch test (L^3)

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Table 1. Equations for the homogenous diffusion model (after Roy et al. 1993)

Equation No.	Equation	Role
2	$\frac{dC_b}{dt} = -M \frac{dq_{avg}}{dt}$	Mass balance for closed batch test
3	$q_{avg} = \frac{3}{(d_p/2)^3} \int_0^{d_p/2} q(r,t) r^2 dr$	Average carbon
4	$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right)$	Diffusion equation for a spherical particle
5	$q(r,0) = 0$	Initial condition
6	$\frac{\partial q}{\partial r} = 0$ for $r=0$	Boundary condition for contin
7	$\rho_p D_s \frac{\partial q}{\partial r} = K_f (C_t - C_s)$	Boundary condition for continuity of flux at $r=d_p/2$
8	$q_s = KC_s^n$	Freundlich isotherm for equilibrium at solid-liquid interface

Figure Captions

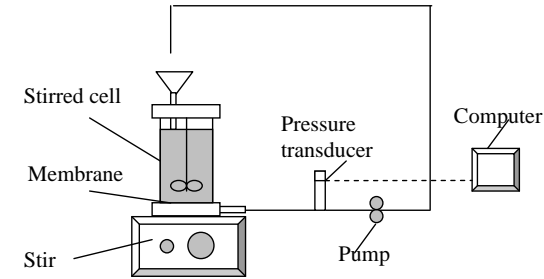


Figure 1. Schematics of the stirred cell system used.

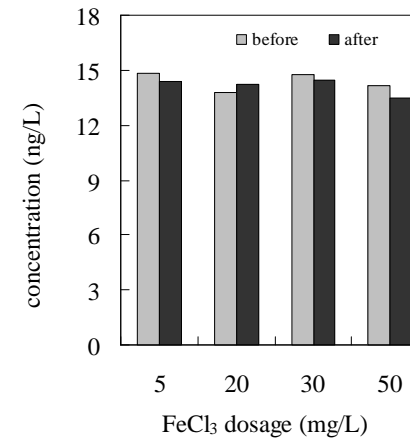


Figure 2 a. Estrone concentrations before and after addition of different doses of ferric chloride (pH=7.49).

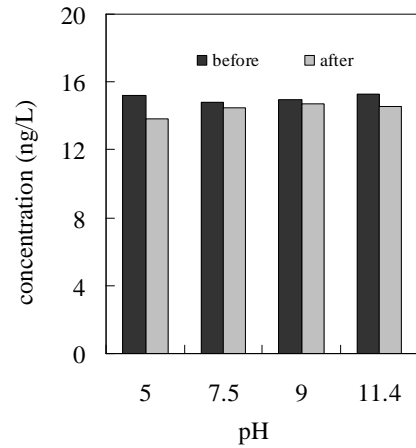


Figure 2 b Estrone concentrations before and after addition of hydrolysable metal salt for different initial pH conditions (dosage: 30 mg/L)

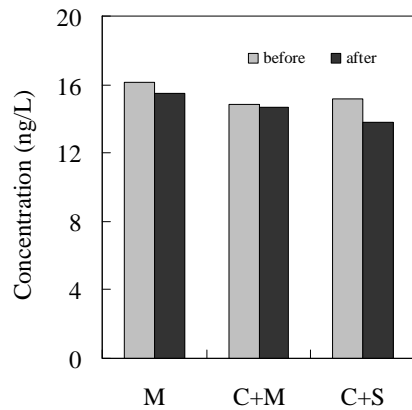


Figure 3 Estrone concentrations after being treated by different processes. (M: membrane filtration; M+C: membrane filtration +coagulation; C+S: coagulation +settling)

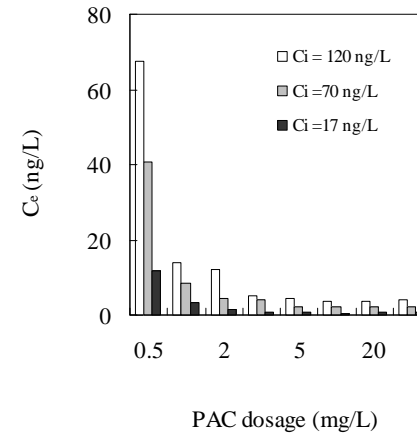


Figure 4. Final (equilibrium) estrone concentrations obtained following addition of a range of doses of powdered activated carbon (PAC) for initial estrone concentrations of 17, 70 and 120 ng/L.

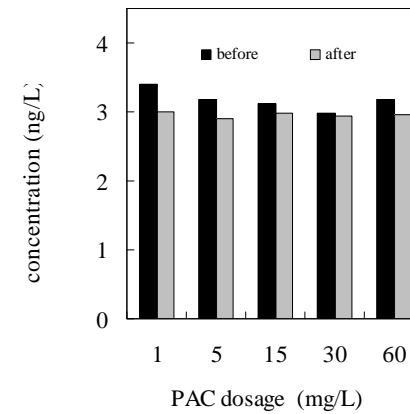


Figure 5. Initial and final estrone concentration following a second addition of PAC (in carbonate buffer solution).

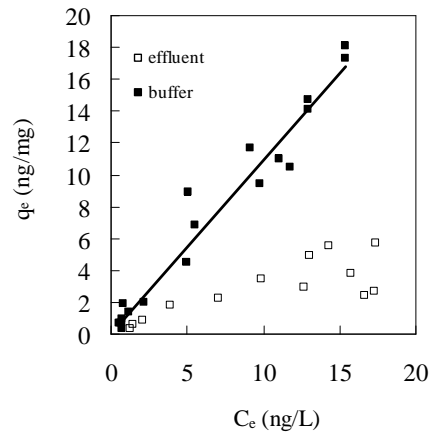


Figure 6. Isotherm equilibrium relationships for estrone adsorption on PAC in carbonate buffer solution and secondary effluent.

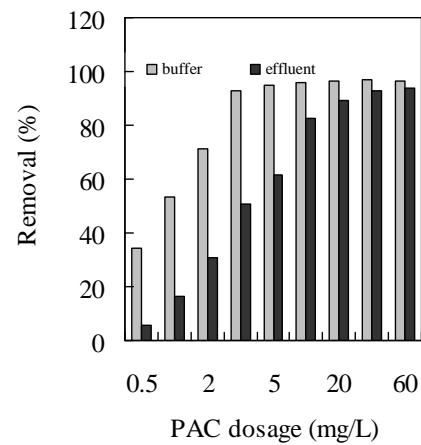


Figure 7. Comparison of the percentage removal of estrone from carbonate buffer and secondary effluent for different doses of PAC.

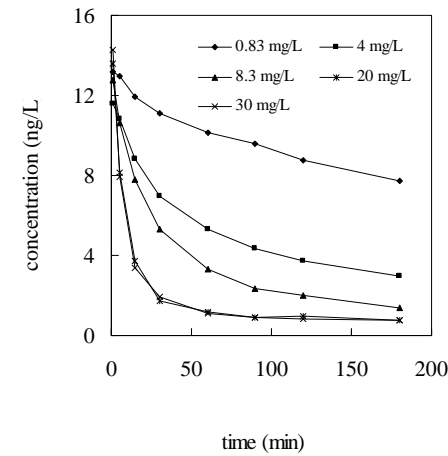


Figure 8. Change in estrone concentration in permeate following addition of different doses of PAC into the stirred cell.

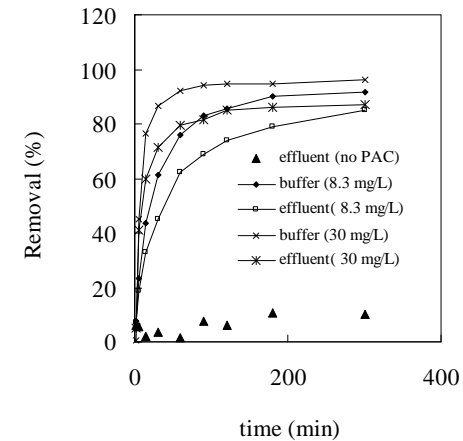


Figure 9. Estrone removal from the secondary effluent and carbonate buffer solution in the absence and presence of different doses of PAC.

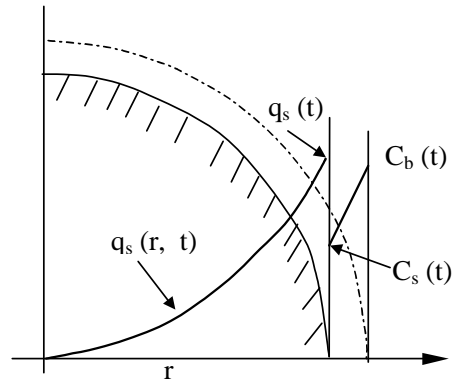


Figure 10. Schematic of mass transfer processes operating in activated carbon adsorption.

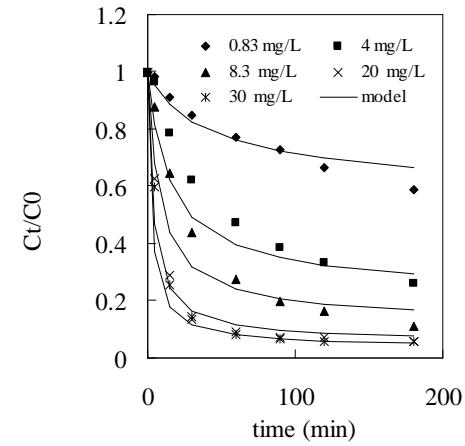


Figure 11 b. Experimental and simulated C_t/C_0 -t relationships (film and surface diffusion limitation model).

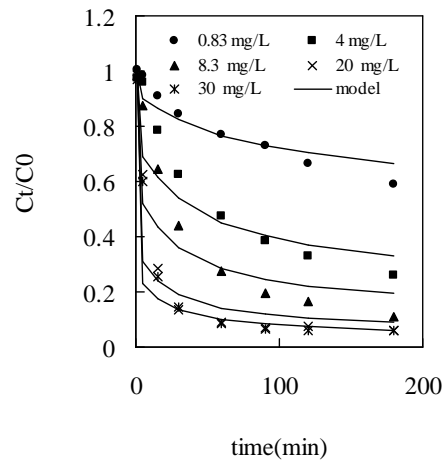


Figure 11 a. Experimental and simulated C_t/C_0 -t relationships (no-film diffusion limitation model).

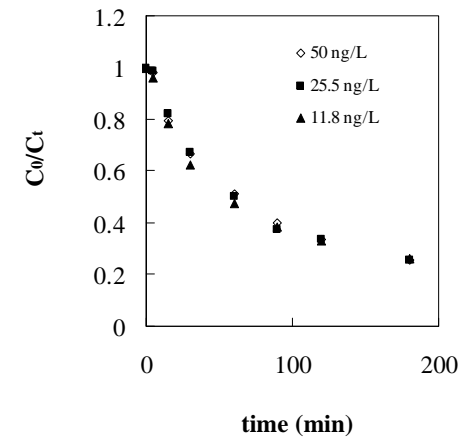


Figure 12. Experimental C_t/C_0 -t relationships for different initial estrone concentrations.